

COPPER ALLOY AND PRODUCING METHOD THEREFOR

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a copper alloy for use in connector materials, etc. More particularly the present invention provides a producing method for a copper alloy in which excellent bendability and strength are obtained simultaneously.

2. Description of Related Art

[0002] A copper alloy that contains titanium (hereinafter called "titanium-copper") is used for connector materials, etc., and in recently, demands therefore have progressively increased. In order to cope with this trend, various research and development concerning precipitation hardening of the titanium-copper has been performed.

[0003] Moreover, in conventional titanium-copper, in some cases, for example, Ni and Al are added (for example, see Japanese Laid-Open Patent Publication No. SHO 50-53228 (pages 1 and 2)), in other cases, Al and Mg are added (for example, see Japanese Laid-Open Patent Publication No. SHO 50-110927 (Pages 1 and 2)), and in other cases, Sn, Ni and Co are added (for example, see Japanese Laid-Open Patent Publication No. SHO 61-223147 (pages 1 to 3)). In addition, in recent years, copper alloys to which Cr, Zr, Ni and Fe are added have been proposed (for example, see Japanese Laid-Open Patent Publication No. HEI 6-248375 Pages 2 to 8)). Moreover, techniques concerning refined crystal grains have been proposed (for example, see Japanese Laid-Open Patent Publication No. 2001-303158 (pages 2 to 4)). Furthermore, techniques for adding Zn, Cr, Zr, Fe, Ni, Sn, In, P and Si to titanium-copper have been proposed (for example, see

Japanese Patent Application No. 2002-31219).

[0004] From the titanium-copper, a supersaturated solid solution is generated by solution treatment, and when it is subjected to aging from this state, a modulated structure which is in a as being metastable phase develops from the initial state, and it stiffens remarkably at a certain time during its development stage. When the modulated structure is over-developed, the titanium-copper is in a so-called over-aged state, and finally, TiCu_3 as a stable phase is precipitated. When the phase increases, the titanium-copper is conversely softened. In this series of aging processes, a modulated structure with high strength is a change which is capable of being generated from an unstable supersaturated solid solution, and the change is not generated from the TiCu_3 phase which is the stable phase toward the modulated structure which is the metastable phase. On the other hand, when the solution treatment is not sufficient, the titanium which cannot be entered into solid solution for the matrix remains as TiCu_3 in the state precipitated. Consequently, in order to fully stiffen by aging, it is necessary to remove the TiCu_3 phase completely in the solution treatment in the beginning process. In other words, it is necessary for the titanium to be entered into the solid solution within the matrix completely. For this reason, it is necessary to heat the object up to a temperature at which the solid solubility of the titanium exceeds the titanium content. For instance, when 3% of the titanium is contained in the copper, it is necessary for the object to undergo solution treatment by heating up to a temperature not less than 800°C in order to dissolve the titanium completely. In addition, like other metallic materials, the titanium-copper is capable of improving its yield strength in such a manner that crystal grains are refined in the annealing process. When producing the titanium-copper, a

recrystallization annealing process as the general final producing process corresponds to a solution treatment, and therefore the primary factor of the yield strength is how to attain refined crystal grains during this solution treatment.

[0005] However, in a conventional high temperature range in which the titanium is completely dissolved, since coarsening of crystal grains easily occurs, in order to attain yield strength improvement due to refined the crystal grains, the solution treatment should be performed at a lower temperature than the above high temperature range. For instance, in an alloy which is made in such a way as to contain 3% titanium in copper, since crystal grains are not refined at 800°C, crystal grains are refined by performing a solution treatment at 750 to 775°C. For that reason, when crystal grains of the titanium-copper are refined by the conventional technique, the titanium is not sufficiently dissolved, so that TiCu_3 which is the stable phase separates out. As described above, there was a problem in that TiCu_3 separated out at the grain boundary at this time, and not only does it not contribute to hardening in the annealing in the post-process, but also, its bendability deteriorates. In addition, in one conventional technique, the third elements (Ni, Al, Mg, Sn, Co, Cr, Zr, Fe, Zn, In, Mn, P, Si, V, Zr or B) are added to the titanium copper. It is an object to bring about precipitation hardening due to precipitation of the second-phase particle containing these components. However, when securing sufficient addition amount of elements for the precipitation hardening, there were problems in that formation of the modulated structure was blocked. In addition, there was a discrepancy between the dissolved condition and the annealing condition to cause precipitation hardening of these elements to the fullest extent, and dissolved condition and annealing condition to

increase strength due to the modulated structure of original titanium-copper to the fullest extent was difficult. Accordingly, it was not possible to sufficiently cope with both the precipitation hardening of the third elements and development of the modulated structure of the titanium-copper. Thus, in the conventional technique, excellent strength characteristics of the titanium-copper are utilized as is, and development of techniques for obtaining greater strength is necessary.

SUMMARY OF THE INVENTION

[0006] The present invention was made in consideration of the above requirement, and it is an object of the present invention to obtain excellent bendability while suppressing precipitation of TiCu_3 , and to achieve further strength improvement in such a manner as to secure excellent characteristics which are sufficient in view of essential qualities of strength of titanium-copper.

[0007] The copper alloy of the present invention contains 2.0 to 4.0 mass% of Ti, 0.01 to 0.50 mass% of one or more than one from among Fe, Co, Cr, V, Zr, B and P as the third element group, and not less than 50% total of the third element as the second-phase particle.

[0008] In the present invention, the content of Ti is 2.0 to 4.0 mass%. In the case in which the content of Ti is less than 2.0%, since it is not possible to sufficiently obtain strength due to formation of the modulated structure of the original titanium-copper, it is not possible to obtain excellent strength in the titanium-copper. In addition, in the case in which the content of Ti is more than 4.0 mass%, TiCu_3 is easily precipitated, deteriorating strength and bendability. In the present invention, the content of Ti is controlled appropriately as described above, so that it is

possible to obtain both excellent strength and bendability. In addition, it is more preferable that, in order to cope with both the strength and bendability at the higher level, the content of Ti be 2.5 to 3.5 mass%.

[0009] In the present invention, there is defined the composition of the element (the third element group) constituting the second-phase particle for the purpose of encouraging sufficient dissolving in the solution treatment and to suppress acceleration of precipitation of TiCu_3 and grain growth. Here, the second-phase particle is a Cu-Ti-X system particle which is generated in the case in which Cu and Ti are taken to as principal components and the third element group constituent element X (specifically, Fe, Co, Ni, Cr, V, Zr, B and P) is contained. This Cu-Ti-X system particle is capable of being generated also in the case in which annealing is performed during solution treatment or before solution treatment, and the Cu-Ti-X system particle contributes to suppression of grain growth after recrystallization. In addition, the Cu-Ti-X system particle is thermally stable; therefore, its shape hardly changes even though cold rolling and/or aging are performed during remaining processes until the product is obtained after solution treatment. In the case in which the total content of Fe, Co, Ni, Cr, V, Zr, B and P is less than 0.01 mass%, since a sufficient amount of the second-phase particles are not precipitated, suppressing effect of crystal grain growth at the time of solution treatment is small. In contrast, in the case in which the total content of Fe, Co, Ni, Cr, V, Zr, B and P exceeds 0.50 mass%, the second-phase particles easily undergo coarsening of crystal grains, and therefore bendability deteriorates. In the present invention, it is possible to obtain especially superior bendability in such a manner as to appropriately control the addition amount of the above-described third element group.

[0010] However, even though the content of the above-described third element group is not controlled properly, if the third element group is not precipitated as the second-phase particle, since the suppressing effect on grain growth is small, coarsening of the crystal grain occurs at the time of solution treatment, so that strength improvement is not expected. In addition, in the condition in which the third element group enters into a solid solution in the matrix, when performing annealing, disturbances occur in formation of modulated structure, so that the hardening degree deteriorates. Consequently, it is necessary that at least half of the content of Fe, Co, Ni, Cr, V, Zr, B and P exist as the second-phase particle. In the present invention, since the content for the second-phase particle of the third element group is controlled properly in such a manner that not less than 50% of the content of the third element group exists as the second-phase particle, it is possible to obtain simultaneously both excellent bendability and strength improvement at a high level.

[0011] Furthermore, another copper alloy of the present invention contains 2.0 to 4.0 mass% of Ti and 0.01 to 0.50 mass% of one or more than one kinds of elements from among Fe, Co, Ni, Cr, V, Zr, B and P as the third element group. Moreover, in the second-phase particle with an area of not less than $0.01 \mu\text{m}^2$ observed by a cross section speculum, the percentage of the number of the second-phase particles in which the content of the third element group within the second-phase particles is not less than 10 times the content of the third element group within the alloy, is not less than 70% of the entire second-phase particle.

[0012] This copper alloy of the present invention, like the above-described copper alloy, is capable of yielding simultaneously both the excellent bendability and strength improvement by achieving proper

control of content of Ti, and proper control of the content of the third element group. However, in the present invention, as described above, it is necessary to properly control the content of the third element group entering into the second-phase particle. In the present invention, in the second-phase particle with an area of not less than $0.01\ \mu\text{m}^2$ observed by a cross section speculum, the percentage of the number of the second-phase particle in which the content of the third element group within the second-phase particles is not less than 10 times the content of the third element group within the alloy, is not less than 70% of the entire second-phase particle, and due to this proper control of the content of the third element group is achieved. For this reason, also in the copper alloy of the present invention, it is possible to simultaneously obtain both excellent bendability and strength improvement at a high level.

[0013] Next, another copper alloy of the present invention contains 2.0 to 4.0 mass% of Ti, and 0.01 to 0.50 mass% of one or more than one kinds of elements from among Fe, Co, Ni, Cr, V, Zr, B and P as the third element group, and the second-phase particle with an area of not less than $0.01\ \mu\text{m}^2$ of area percentage A_f observed by a cross section speculum is not more than 1.0%.

[0014] In the present invention, 2.0 to 4.0 mass% of Ti is contained. In the case in which the content of the Ti is less than 2.0%, sufficient strength cannot be obtained due to the formation of a modulated structure of the original titanium-copper, it is not possible to obtain excellent strength of the titanium-copper. In contrast, in the case in which the content of Ti exceeds 4.0 mass%, TiCu_3 is easily precipitated, so that bendability deteriorates. In the present invention, it is possible to obtain both excellent bendability and strength by properly controlling the content of Ti

as above. In addition, it is more preferable that, in order to cope with both the strength and bendability at a higher level, the content of Ti be 2.5 to 3.5 mass%.

[0015] The present invention adds the third element to form the second-phase particle; however, the object of the second-phase particle is not precipitation hardening occurrence as in the conventional technique, but to suppress the growth of the crystal grains. Consequently, the third element group stipulated in the present invention is not the particle with high precipitation hardening property, but is the elements to produce the particle which can suppress effects of growth of the crystal grains. Such a third element group is selected carefully after extensive experimentation on the elements. Here, the second-phase particle is a Cu-Ti-X system particle which is generated in the case in which Cu and Ti are taken to as principal components and the third element group constituent element X (specifically, Fe, Co, Ni, Cr, V, Zr, B and P) is contained. This Cu-Ti-X system particle is capable of being generated also in the case in which annealing is performed during solution treatment or before solution treatment and the Cu-Ti-X system particle contributes to suppressing the grain growth after recrystallization. In addition, the Cu-Ti-X system particle formed by the third element group stipulated in the present invention is thermally stable; therefore, its shape hardly changes even though cold rolling and/or aging are performed during remaining processes until the product is obtained after solution treatment. In the case in which the total content of Fe, Co, Ni, Cr, V, Zr, B and P is less than 0.01 mass%, since a sufficient amount of the second-phase particle is not precipitated, suppressing effects of crystal grain growth at the time of solution treatment is small. In contrast, in the case in which the total content of Fe, Co, Ni,

Cr, V, Zr, B and P exceeds 0.50 mass%, the second-phase particles easily undergo coarsening of crystal grains during solution treatment; therefore, bendability deteriorates, so that there occurs the adverse effect of deteriorated bendability. In the present invention, it is possible to obtain particularly excellent bendability in such a manner by properly controlling the addition amount of the above-described third element group.

[0016] However, even though the content of the above-described third element group is controlled properly, over-annealing causes the second-phase particles to be precipitated excessively, so that bendability deteriorates; therefore, it is necessary for the precipitation amount of the second-phase particle to be limited. In the present invention, the area percentage Af of the second-phase particle with not less than $0.01\ \mu\text{m}^2$ area observed by a cross section speculum is made to not be more than 1.0%. Here, the above-described area percentage Af is the total area percentage of the second-phase particle per unit area; more specifically, it means the occupied rate of the total of the area of the second-phase particle is the physical object measured in the visual field area of the titanium-copper. This area percentage Af is observed in such a manner as to observe a test material cross section with a scanning electron microscope, etc., and it is possible to measure it by image processing. In the case in which the value of this area percentage Af exceeds 1.0%, it is a condition in which the second-phase particle is precipitated excessively, so that bendability deteriorates. In the present invention, it is possible to obtain especially excellent bendability by properly controlling the above described area percentage Af.

[0017] As indicated above, according to the present invention, it is possible to provide a copper-alloy having simultaneously both excellent

bendability and strength by stipulating the content amount of Ti and by stipulating the composition of the content amount of the third element group and the area percentage A_f of the second-phase particle.

[0018] In addition, another copper alloy of the present invention contains 2.0 to 4.0 mass% of Ti, and 0.01 to 0.50 mass% of one or more than one kind of element from among Fe, Co, Ni, Cr, V, Zr, B and P as the third element group, and concerning the second-phase particle with an area of not less than $0.01 \mu\text{m}^2$ observed by the cross section speculum, equable dispersion degree E defined by the formula below is not more than 0.8

$$E = \frac{\sqrt{\frac{1}{n} \sum_i^n (d_i - \sqrt{A_0/N_A})^2}}{\sqrt{\frac{A_0}{N_A}}}$$

d_i is the distance from the i -th second-phase particle to the nearest second-phase particle

A_0 is the measured visual field area

N_A is the number of the second-phase particles observed within the measured visual field area.

[0019] The requirements of this copper alloy of the present invention are that, like the above-described copper alloy, it is possible to simultaneously obtain both excellent bendability and strength improvement by achieving proper control of the content of the Ti and proper control of the content of the third element group. However, although the content of the above-described third element group is controlled properly, if the second-phase particle formed by this means is not dispersed homogeneously, it is not possible to efficiently suppress grain growth during recrystallization annealing, so that it is not possible to obtain excellent bendability. In addition, if the second-phase particle is not

dispersed homogeneously, constituents are easily mixed with grains. When executing plastic formation such as bending deformation or tensile force on an alloy whose constituents are duplex grains structure, deformation amounts within constituents are not even, so that differences occur from one locality to another. Specifically, the larger the grain and the fewer the second-phase particles, the more the copper alloy is easy to deform, while in the converse case, the copper alloy is difficult to deform. That is, in the case of macroscopic forming, partial deformation amount is focused on the deformable portion, and crack propagation occurs from its point; therefore, if the constituents are duplex grains structure, one in which large grains and small grains are mixed, even though average crystal grain diameter is small, the bendability and strength deteriorate in comparison with the constituent of unclumped grains with the same grain diameter. In the present invention, concerning the second-phase particle with an area of not less than $0.01 \mu\text{m}^2$ observed by a cross section speculum, equable dispersion degree E is taken to be not more than 0.8. The equable dispersion degree E indicates that the closer the value is to zero, the more the second-phase particle is dispersed homogeneously, and conversely, the equable dispersion degree E indicates that the larger the value, the more the dispersion has bias was discussed. Here, the equable dispersion degree E is an entirely new statistic which was discovered by the present inventors. Heretofore, there is no example of a quantitative evaluation being performed about the influence which the second-phase particle distribution exerts on the distribution of crystal grains or mechanical characteristics, and there is also no example that homogeneousness as such of the second-phase particle distribution is made by performing quantitative evaluation. However, the present inventors found that even if the total

number or area percentage of the second-phase particles is identical with each other, if the distribution condition is different, constituents and/or mechanical characteristics differ, with the result that, in particular, the inventors noticed distribution conditions of the second-phase particles and examined this continuously during the course of examining crystal constituents and mechanical characteristics of various test materials. Furthermore, the relationship between the distribution of the second-phase particle and constituents or mechanical characteristics was repeatedly researched in detail from various angles, with the result that the more the second-phase particle is dispersed homogeneously, the more the crystal grains were not clumped, so that excellent bendability and high yield strength are obtained. Consequently, the inventors considered whether or not it is possible to perform quantitative evaluation about homogeneousness of the grain distribution. As a result, the statistic with its reasonableness is the equable dispersion degree E. When this value E exceeds 0.8, there is considerable bias in distribution of the second-phase particle, so that it became clear from the experimental data that it is not possible to obtain both excellent bendability and strength. In the present invention, it is possible to obtain both the excellent in bendability and strength in such a manner as to achieve proper control of the above-described equable dispersion degree E.

[0020] Moreover, a producing method of the copper alloy of the present invention is a method for preferably producing the above-described two copper alloys of the present invention which comprises a process for producing an ingot in which 0.01 to 0.50 mass% of one or more than one kind of element from among Fe, Co, Ni, Cr, V, Zr, B and P is added to Cu, and after that 2.0 to 4.0 mass% of Ti is added, and a process for producing

a solid solution in the case of heating the ingot up to an ultimate temperature $T^{\circ}\text{C}$, in such a manner as to heat the ingot up to temperature exceeding 600°C with a heating rate of not less than $20^{\circ}\text{C}/\text{sec}$, and thereafter, heating the ingot for not less than 10 sec within the temperature range of $T-100^{\circ}\text{C}$ to $T^{\circ}\text{C}$, a process for producing rolled material being applied to the cold-rolling of 5 to 50% to the solid solution and a process for applying aging to the rolled material at 350 to 450°C .

[0021] According to the producing method of the copper alloy of the present invention, it is possible to simultaneously attain both excellent bendability and strength improvement by achieving proper control of the addition amount of the Ti and proper control of the addition amount of the third element group.

[0022] However, as described above, even though the proper control of the addition amount of the Ti and the proper control of addition amount of the third element group are achieved, if the proper control of content of the third element group for the second-phase particle is not achieved, it is not possible to obtain the required bendability and strength. According to Zener theory which clarifies relationship between the second-phase particle and the re-crystal grain growth, the more the second-phase particle is dispersed homogeneously and finely, the larger is the effect of suppressing grain growth. For instance, in Japanese Laid-Open Patent Publication No. SHO 58-220139, based on this Zener theory, there is disclosed a technique in which the second-phase particle is made to be finely dispersed before re-crystallization annealing process. In contrast, the present inventors found that it is possible to cope with both the bendability and the strength at a high level by sufficiently refining the crystal grain under conditions of completely dissolving the titanium in such a manner as to finely disperse

the second-phase particle in the initial stage of solution treatment corresponding to just a re-crystallization annealing process, not before re-crystallization annealing. Specifically, the inventors completed the present invention by finding that it is possible to obtain the above-described effects by achieving proper control of the heating rate in the solution treatment. That is, in the present invention, the ultimate object is obtained in such a manner as to heat the material up to a temperature exceeding 600°C with the heating rate being not less than 20°C/sec. In the case in which this heating rate is less than 20°C/sec, it is not possible to suppress precipitation of the TiCu_3 phase, and for this reason, the bendability deteriorates. In the copper alloy of the present invention, it is possible to simultaneously obtain both the excellent bendability and strength improvement at a high level by achieving proper control of the above-described heating rate.

Preferred Embodiments of the Invention

[0023] Copper alloys of the present invention in accordance with its producing process will be described sequentially below. In addition, the producing method comprised of processes shown below is one producing example of the copper alloy of the present invention.

[0024] Embodiment 1

Ingot Producing Process

As the third element group, 0.01 to 0.50 mass% of one or more than one kind of element from among Fe, Co, Ni, Cr, V, Zr, B and P was added to an adequate amount of Cu, and thereafter, maintaining them sufficiently, and then 2.0 to 4.0 mass% of Ti was added. In order to effectively liberate the third element group as the second-phase particle, it was

necessary to maintain sufficiently the third element group after addition in order to eliminate insoluble residue of the third element group at the ingot producing process. In addition, the Ti is more easily dissolved than the third element group, and therefore the Ti may be added after dissolution of the third element group.

[0025] Process after Ingot Producing

It is desirable to perform homogenizing annealing for not less than one hour at not less than 950°C after this ingot producing process. By this, segregation is reduced, and in the solution treatment described later, it causes precipitation of the second-phase particle to disperse finely and homogeneously, and it is also possible to prevent occurrence of duplex grains structure. Subsequently, hot-rolling is performed, and then the solution treatment is performed while repeating the cold-rolling and the annealing. The second-phase particle is formed in the annealing process when the annealing temperature is low, and therefore, the annealing is performed at the temperature in which the second-phase particle is completely dissolved. In the case of regular titanium-copper to which the third element group is not added, its temperature may be taken to as high as 800°C. It is desirable that the annealing temperature be taken to as high as not less than 900°C in the case of the titanium-copper to which the third element group is added. Moreover, in the cold-rolling process just before the solution treatment, the higher the degree of processing, the more the precipitation of the second-phase particle in the solution treatment is made homogeneous and fine. In addition, in order to precipitate the fine second-phase particle before the solution treatment, annealing may be performed at low temperatures after the above described cold-rolling; however, only small effects were obtained; therefore, it is not advisable in

consideration of cost increases because of process increases. When performing low temperature annealing before solution treatment for the above-described object, it is desirable to perform the low temperature annealing at a temperature of not more than 450°C under which Ostwald growth of the second-phase particle is unlikely to occur.

[0026] Solution Treatment Process

The solution treatment is performed after the above-described cold-rolling plate producing process. Here, note that it is necessary to heat it up to a temperature (730 to 840°C with 2 to 4 mass% of Ti added, for example, 800°C at 3 mass% of Ti added) at which Ti solid solubility is larger than the added. In its heating rate, in order to rapidly pass through a temperature range where TiCu_3 is easiest to be precipitated, at least up to 600°C, the heating rate should be set to not less than 20°C/sec. According to proper control of this heating rate, it is possible to improve bendability while suppressing precipitation of TiCu_3 to be the stable phase, and it is possible to generate the fine and homogenous second-phase particles in such a manner that the second-phase particles with high suppressing effect against growth of the recrystallized grains, that is the third element, is taken as main component.

[0027] Cold-rolling Process / Aging Treatment Process

The cold-rolling and aging treatment are performed sequentially after the above-described solution treatment process. These processes are capable of being performed by regular methods and under conditions, depending on the application of the copper alloy. For example, when the copper alloy is used as connector material, etc., regarding the cold-rolling, it is desirable that 5 to 50% cold-rolling be applied to the solid solution. In addition, regarding the aging treatment, it is desirable that an aging

treatment of a degree of 200 min be performed in an inert atmosphere, such as Ar gas, at 400°C.

[0028] Embodiment 2

Ingot Producing Process

As the third element group, 0.01 to 0.50 mass% of one or more than one kind of element from among Fe, Co, Ni, Cr, V, Zr, B and P is added to a prescribed amount of Cu, and thereafter, maintaining them sufficiently, and then 2.0 to 4.0 mass% of Ti is added. In order to effectively liberate the third element group as the second-phase particle, it is necessary to maintain sufficiently the third element group after addition in order to eliminate insoluble residues of the third element group in the ingot producing process. In addition, the Ti is easily dissolved in the Cu, and therefore the Ti may be added after addition of the third element group.

[0029] It is desirable to perform homogenizing annealing for not less than ten hours at not less than 950°C after this ingot producing process. By doing so, segregation is reduced, and in the solution treatment described later, it causes precipitation of the second-phase particle to disperse finely and homogeneously, and it is also possible to prevent the occurrence of duplex grains structure. That is, if the homogenizing annealing is performed sufficiently, it is possible for the above described equable dispersion degree E to be not more than 0.8. For that reason, it is possible to disperse the second-phase particle homogeneously as desired, so that it is possible to attain especially excellent bendability. In addition, it is possible to prevent the second-phase particle from being precipitated as rough and large precipitates in later solution treatment by performing sufficient homogenizing annealing. In other words, it is possible to disperse finely the second-phase particle as desired, so that it becomes possible to

prevent duplex grains structure. Subsequently, hot-rolling is performed, and then the solution treatment is performed while repeating the cold-rolling and the annealing. The second-phase particle is formed in the annealing process when the annealing temperature is low, and therefore, the annealing is performed at the temperature at which the second-phase particle is dissolved completely. In the case of regular titanium-copper to which the third element group is not added, the temperature may be 800°C. It is desirable that the annealing temperature be not less than 900°C in the case of the titanium-copper to which the third element group is added. Moreover, in the cold-rolling process just before the solution treatment, the higher the degree of processing, the more the precipitation of the second-phase particle in the solution treatment is made homogeneous and fine. In addition, in order to precipitate the fine second-phase particle before the solution treatment, annealing may be performed at low temperature, after the above described cold-rolling; however, only small effects are obtained, and therefore, it is not advisable in consideration of increase cost due to increased processing. If low temperature annealing is performed before solution treatment for the purpose of precipitating the minute second-phase particle before solution treatment, it is desirable to perform the low temperature annealing at a temperature not greater than 450°C under which rough and large crystal grains are not generated.

[0030] Solution Treatment Process

The solution treatment is performed after the above-described ingot producing process. Here, note that it is necessary to heat it up to a temperature (730 to 840°C with 2 to 4 mass% of Ti added, for example, 800°C at 3 mass% of Ti added). In the process of heating rate, in order to rapidly pass through a temperature range where TiCu_3 is easiest to

precipitate, at least up to 600°C, the heating rate should be set to not less than 20°C/sec. According to proper control of this heating rate, it is possible to improve bendability while suppressing precipitation of TiCu₃ to be the stable phase, and it is possible to generate the fine and homogenous second-phase particles in such a manner that the second-phase particles with high suppressing effect against growth of the recrystallized grains, namely the third element, is the main component. In addition, due to proper control of the above described heating rate and heating time, it is possible to make the area percentage Af of the second-phase particle of not less than 0.01 μm² area observed by a cross section speculum to be not more than 1.0%. By doing so, it is possible to obtain especially superior bendability without precipitating the second-phase particles excessively.

[0031] Cold-rolling Process / Aging Treatment Process

The cold-rolling and aging treatment are performed sequentially after the above-described solution treatment process. These processes are capable of being performed by regular methods and conditions, depending on the application of the copper alloy. For example, when the copper alloy is used as a connector material, etc., regarding the cold-rolling, it is desirable that 5 to 50% cold-rolling be applied to the solid solution. In addition, regarding the aging treatment, it is desirable that an aging treatment for 100 to 1000 minutes be performed in an inert atmosphere, such as Ar gas, at 350 to 450°C.

Embodiments

[0032] Next, there will be described embodiments of the present invention.

[0033] In the case of the copper alloy of the present invention, a vacuum

melting furnace is used for ingot producing in consideration of the fact that active Ti is added as the second component. In addition, in order to prevent the occurrence of unexpected adverse effects caused by interfused impurities other than those stipulated elements in the present invention, high-grade raw material (electrolytic copper and pure titanium) is used.

[0034] Verification Example 1

First, as to Embodiments 1 to 10 and Comparative Examples 11 to 20, respective Fe, Co, Ni, Cr, V, Zr, B and P are added to Cu with compositions as shown in Table 1, and then, Ti of compositions indicated in the same table is added. In order to produce conditions in which there is no undissolved residue of the added element, the holding time after addition is taken into consideration sufficiently, and after that, these are implanted into a casting mold in an Ar atmosphere, and then 2kg ingots are made.

[0035] Table 1

(Unit of content of each element is mass %)

	No.	Fe	Co	Ni	V	Zr	Cr	P	B	Ti	Heating rate (°C/sec)
Embodiment	1	0.1								2.4	150
	2		0.1							2.3	160
	3			0.2						3.6	30
	4	0.1						0.03		3.1	100
	5		0.1					0.04		3.2	80
	6			0.2				0.05		2.7	140
	7				0.2					3.3	90
	8					0.1	0.2			2.9	130
	9				0.2				0.02	3.2	40
	10					0.1	0.2		0.02	3.0	120
Comparative Example	11	0.1								1.5	110
	12		0.1							5.0	120
	13									3.0	130
	14	1.0								3.0	40
	15	0.5	0.5					0.2		3.0	50
	16					0.5	0.5		0.3	3.0	150
	17	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	2.9	140
	18	0.2	0.1							2.8	5
	19		0.1	0.3						3.1	7
	20				0.3				0.1	3.2	9

[0036] Oxidation inhibitor is applied to the above ingot. After 24 hours drying at room temperature, hot rolling is applied thereto by heating of

950°C for 2 hours, so that a hot rolling plate with a thickness of 10 mm is obtained. Next, in order to suppress segregation, the oxidation inhibitor is applied again to the hot rolling plate, then heating at 950°C for 2 hours is applied, and afterwards, water quenching is performed. In addition, the reason why the oxidation inhibitor is applied is to prevent at both grain boundary oxidation and internal oxidation, by which intercalated objects may be generated in such a manner as to react oxygen entered from the surface and added element component. Each hot rolling plate is subjected to cold rolling coming to a thickness of 0.2 mm after descaling by mechanical grinding and acid pickling. Afterwards, the rolled material being subjected to cold rolling is inserted into an annealing furnace capable of heating rapidly to heat at a heating rate shown in table 1 up to a temperature exceeding 600°C. Ultimately, the rolled material is heated up to a temperature (800°C in the case in which the added amount of Ti is 3 mass%) at which Ti solid solubility becomes larger than the added amount, and then water cooling is applied thereto after holding for two minutes. On this occasion, average crystal grain size (GS) is measured by the intercept method. Afterwards, there is obtained rolled material with a thickness of 0.14 mm while applying cold rolling after pickling. Test pieces of respective Embodiments and Comparative Examples are formed in such a manner as to heat the rolled material described above to 400°C for 3 hours in an inert gas atmosphere.

[0037] Next, as to respective Embodiments and respective Comparative Examples, there is measured MBR/t value, which is the ratio between the minimum bending radius (MBR) at which cracking does not occur while performing a W bending test in the rolling direction and transverse direction (the bending axis is the same direction as the rolling direction),

and the thickness (t). Effectiveness of the embodiments is verified while measuring 0.2% yield strength.

[0038] Moreover, verification of composition of the second-phase particle is performed by the following two methods. The adopted first valuation method is that a test piece of a certain weight is dissolved in phosphoric acid, and the obtained liquid is filtered by a membrane filter (0.1 μm mesh) to separate the second-phase particles, and then the remaining solution component is subjected to quantitative analysis, and by this means, the rate at which the third element group exists as the second-phase particle is calculated. By this method, the calculated value is taken to as A value (%) as a matter of convenience. It is indicated that the higher the A value, the higher the rate at which the third element group added by the present invention as the second-phase particle exists, if the A value is 100%, and it indicates that all the third element group exists as the second-phase particle. Practically, the mesh size of the filter is finite, and therefore, it is impossible to precipitate to separate the entirety of the second-phase particles. However, there may be adopted the method for analyzing the remaining solution in which the not separated second-phase particles are contained, and therefore, if this value is not less than 50%, a real A value exceeds 50% inevitably, and this means that it is included in the present invention. The adopted second valuation method is that the entire composition of the second-phase particle of a length not less than 0.1 μm per unit area is measured by field-emission type Auger electron spectroscopy (FE-AES), in the second-phase particle of not less than 0.01 μm^2 in area, there is obtained the rate to the measured total number of particles while counting the number of the particle that the content of the third element group within the second-phase particle is not less than 10

times the content of the third element group within the alloy. This value is taken as the B value as a matter of convenience. Furthermore, there is estimated the rate of the third element group existence as the second-phase particle from the relationship between each particle area and its composition, while finding the corresponding circular diameter of the second-phase particle. It is verified that if the measurement field of view area is secured sufficiently, the test piece alloy which satisfies the A value approximately satisfies the B value. Here, the corresponding circular diameter is the diameter of the circle which has the same area as the second-phase particle observed by the cross section speculum. Table 2 shows the A values, B values, crystal grain sizes (GS), 0.2% yield strengths (Mpa) and MBR/t values of respective Embodiments and respective Comparative Examples.

[0039] Table 2

	No.	A value (%)	B value (%)	GS(μ m)	MBR/t	0.2% yield strength (MPa)
Embodiment	1	66	82	4.2	0.7	852
	2	67	80	4.5	0.7	853
	3	70	85	3.6	1.0	880
	4	71	84	2.5	0.7	875
	5	80	88	2.4	1.0	888
	6	81	87	2.3	1.0	888
	7	85	90	3.2	0.7	873
	8	88	91	3.5	0.7	872
	9	90	92	2.7	0.7	888
	10	91	93	2.8	0.7	889
Comparative Example	11	55	72	4.1	0.7	770
	12	53	75	4.2	3.5	880
	13	-	-	35	2.1	810
	14	70	80	1.5	3.5	822
	15	75	81	1.2	3.5	820
	16	87	90	1.3	4.3	795
	17	90	93	1.2	3.5	854
	18	42	61	3.1	2.1	815
	19	40	56	2.9	2.1	805
	20	35	50	2.7	2.1	812

[0040] As seen in the Examples in Table 2, in the respective Embodiments, in any case, the MBR/t value is not more than 1.0, and the 0.2% yield strength is not less than 850MPa, and there is excellent

bendability and strength obtained simultaneously. In the Embodiments No. 4 to 10, the addition amount of Ti is taken as an especially preferable range (2.5 to 3.5 mass %), and therefore, the 0.2% yield strength is remarkably improved, and its value is not less than 870MPa. In addition, in the Embodiments No. 4 to 6, each of Fe, Co or Ni is added thereto and furthermore P is added to each, and in the Embodiments No. 9 and 10, each of V or Zr is added thereto and furthermore, B is added to each, and therefore, the crystal grains are further refined, so that the 0.2% yield strength is extremely improved, and its value is not less than 875MPa.

[0041] On the other hand, in the respective Comparative Examples, the MBR/t values exceeding 1.0 or the 0.2% yield strength is less than 850MPa, and this shows that excellent bendability and strength are not obtained simultaneously. In the Comparative Example No. 11, since the addition amount of Ti is less than 2.0 mass%, sufficient 0.2% yield strength is not obtained. Conversely, in the Comparative Example No. 12, since the addition amount of Ti exceeds 4.0 mass%, TiCu_3 is precipitated, so that bendability deteriorates. In the Comparative Example No. 13, since the third element group to be an element for refining crystal grain is not added, the crystal grain is not refined, so that sufficient 0.2% yield strength is not obtained. Furthermore, in the Comparative Example No. 13, since the second-phase particle is not formed, the crystal grain becomes rough and large, so that it is again not possible to obtain excellent bendability. In the Comparative Examples Nos. 14 to 17, since the total value of the addition amount of the third element group exceeds 0.5 mass%, the second-phase particle is precipitated more than necessary, so that bendability is deteriorated. In addition, Ti within the matrix is lost because of excessive precipitation of the second-phase particle, and therefore sufficient 0.2%

yield strength is not obtained while reducing age hardening faculty. In the Comparative Examples Nos. 18 to 20, the addition amount of the third element is within the proper range, the heating rate up to the temperature at which Ti is dissolved completely is slow in the solution treatment, and therefore the single precipitation rate of TiCu_3 becomes greater than the second-phase particle with the third element as the main component, and as a result, the age hardening faculty is lowered, so that sufficient 0.2% yield strength is not obtained, and bendability is not within the preferable range.

[0042] Verification Example 2

First, regarding Embodiments Nos. 21 to 30 and Comparative Examples Nos. 31 to 40, respective prescribed amounts of Fe, Co, Ni, Si, Cr, V, Zr, B and P are added to Cu with compositions as shown in Table 3, and afterwards, Ti in amounts corresponding to compositions indicated in the same table are added respectively. In order to make conditions in which there is no undissolved residue of the added elements, the holding time after addition is taken into consideration sufficiently, and after that, these are placed into a casting mold in an Ar atmosphere, and then about 2 kg ingots are made.

[0043] Oxidation inhibitor is applied to the above ingots. After 24 hours of drying at room temperature, hot rolling is applied thereto by heating (homogenization annealing) at 980°C for 12 hours, so that hot rolling plates with thicknesses of 10 mm are obtained. Next, the oxidation inhibitor is applied again to the hot rolling plate, then heating at 980°C for 2 hours is applied, and afterwards, quenching is performed. This is a step for further reducing segregation, and it is the most effective means for dispersing precipitation of the second-phase particle homogeneously. Here, the reason why the oxidation inhibitor is applied is to prevent at best

both grain boundary oxidation and internal oxidation, by which intercalated objects are generated in such a manner as to react oxygen entered from the surface and added element component. In addition, the reason why the quenching is performed is to accelerate the cooling rate after the solution because if the cooling rate is low, the second-phase particle is precipitated excessively. Each hot rolling plate is subjected to cold rolling to a thickness of 0.2mm after descaling by mechanical grinding and pickling. Afterwards, the rolled material being subjected to cold rolling is inserted into an annealing furnace capable of heating rapidly to heat at heating rate of 50°C/sec up to the temperature (800°C in the case in which the addition amount of Ti is 3 mass%) at which Ti solid solubility becomes larger than the addition amount, and then quenching is applied thereto after one minute holding. On this occasion, average crystal grain size (GS) is measured by the section method. Afterwards, there is obtained a rolled material with a thickness of 0.14 mm while applying cold rolling after pickling. Test pieces of respective Embodiments and Comparative Examples are formed in such a manner as to heat the rolled material described above at 400°C for 3 hours in an inert gas atmosphere. Table 3 shows wet quantitative analysis value of the test pieces of these Embodiments Nos. 21 to 30 and Comparative Examples Nos. 31 to 40. In addition, all units concerning indicated values in Table 3 are in mass%.

[0044] In addition, in Comparative Examples Nos. 34 to 40, samples are prepared with conditions described later.

[0045] Table 3

	No.	Ti	Fe	Co	Ni	V	Zr	Cr	P	B	Cu
Embodiment	21	2.3		0.1							residual part
	22	2.4	0.1								residual part
	23	3.6			0.2						residual part
	24	3.1		0.1					0.04		residual part
	25	3.2	0.1						0.05		residual part
	26	2.7			0.2				0.03		residual part
	27	3.3				0.2					residual part
	28	2.9					0.1	0.2			residual part
	29	3.2				0.2				0.03	residual part
	30	3.0					0.1	0.2		0.03	residual part
Comparative Example	31	1.5		0.1							residual part
	32	5.0	0.1								residual part
	33	3.0									residual part
	34	3.0	1.1								residual part
	35	3.0	0.4	0.6					0.2		residual part
	36	3.0					0.5	0.5		0.3	residual part
	37	2.9	0.1	0.3	0.2	0.2	0.1	0.2	0.2	0.2	residual part
	38	2.8	0.1	0.2							residual part
	39	3.1		0.2	0.3						residual part
	40	3.2				0.3				0.1	residual part

[0046] Next, as to respective Embodiments and respective Comparative examples, there is obtained minimum bending radius (MBR) at which cracking does not occur while performing W bending tests as stipulated by JIS 3110 on various prescribed bending radiuses of width 10 mm × length 100 mm in the rolling direction and transverse direction (inferior). The bendability is represented by the ratio (MBR/t) between minimum bending radius MBR and the thickness t. With respect to strength, effectiveness of the Embodiments is verified with a measured 0.2% yield strength. Here, the MBR/t value indicates that the smaller the value, the greater superiority in bendability. In addition, regarding verification of the second-phase particle, with respect to the area percentage Af of the second-phase particles and average dispersion degrees E, images taken of the surface of respective test pieces are analyzed by using image analysis software. Table 4 shows each of Af, E, crystal grain size (GS), MBR/t value and 0.2% yield strength of respective Embodiments and respective Comparative Examples.

[0047] Table 4

	No.	Al(%)	E	GS(μ m)	MBR/t	0.2% yield strength (MPa)
Embodiment	21	0.25	0.53	4.3	0.7	851
	22	0.85	0.43	4.6	0.7	852
	23	0.76	0.38	3.7	1.0	881
	24	0.53	0.56	2.8	0.7	876
	25	0.68	0.61	2.5	1.0	887
	26	0.73	0.73	2.6	1.0	886
	27	0.46	0.53	3.5	0.7	872
	28	0.65	0.58	3.7	0.7	870
	29	0.38	0.53	2.8	0.7	887
	30	0.55	0.51	2.9	0.7	888
Comparative Example	31	0.11	0.45	4.3	0.7	771
	32	1.25	0.53	4.5	3.5	882
	33	0.12	0.88	36	2.1	811
	34	1.54	0.68	1.6	1.4	821
	35	2.65	0.72	1.4	2.1	822
	36	3.76	0.78	1.4	2.8	793
	37	4.87	0.82	1.5	3.5	853
	38	0.82	0.87	3.3	1.4	836
	39	0.78	0.91	2.7	1.4	826
	40	0.97	0.93	2.5	2.1	833

[0048] As seen in the examples in Table 4, in the respective embodiments, in any case, the MBR/t value is not more than 1.0, and the 0.2% yield strength is not less than 850MPa, and this shows that excellent bendability and strength are obtained simultaneously. In particular, in the Embodiments Nos. 24 to 30, Ti is in a more preferable range (2.5 to 3.5 mass%), and therefore, the 0.2% yield strength is further improved than in the other Embodiments, and its value becomes 870MPa. In addition, in the Embodiments Nos. 24 to 26, each of Fe, Co, or Ni is added thereto, and further P is added to each, and in the Embodiments Nos. 29 and 30, each of V or Zr is added thereto, and furthermore, B is added to each, and therefore, the crystal grain is further refined, so that the 0.2% yield strength is extremely improved, and its value is not less than 880MPa.

[0049] On the other hand, in the respective Comparative Examples, the MBR/t values exceed 1.0 or the 0.2% yield strength is less than 850MPa, and this shows that excellent bendability and strength are not obtained simultaneously. Specifically, in the Comparative Example No. 31, since the content of Ti is not more than 2.0 mass%, sufficient 0.2% yield strength,

that is, strength is not obtained. Conversely, in the Comparative Example No. 32, since the content of Ti exceeds 4.0 mass%, the MBR/t value is large, so that excellent bendability is not obtained. In the Comparative Example No. 33, since the element for precipitating the second-phase particle which suppresses growth of crystal grains is not added, the crystal grains are not refined, so that excellent strength is not obtained. Furthermore, in the Comparative Example No. 33, since the crystal grain becomes rough and large, so that it is also not possible to obtain excellent bendability. In the Comparative Examples Nos. 34 to 37, treatment is performed at a temperature at which TiCu_3 is easily precipitated (regarding Comparative Examples Nos. 34 to 37, the solution treatment temperature is 750°C ; in other Embodiments and Comparative Examples, the solution treatment temperature is 800°C). In these Comparative Examples, the area percentage Af of the second-phase particle exceeds 1.0%, and therefore it is not possible to obtain excellent bendability. In addition, Ti within the matrix is lost because of excessive precipitation of the second-phase particle, and therefore sufficient 0.2% yield strength is low, while reducing age hardening faculty, so that it is not possible to obtain excellent strength. The Comparative Examples Nos. 38 to 40 are produced in such a manner as to apply hot rolling without performing sufficient homogenizing annealing while repeating cold rolling and annealing after air-cooling. In these Comparative Examples, the area percentage Af is within a proper range; however, the second-phase particle is not dispersed homogeneously. For that reason, crystal constitution is of duplex grains structure, and it is not possible to obtain excellent bendability and strength.